THE DOUBLE-DUTY ANODE FOR
MOLTEN-CARBONATE FUEL CELLS

R. W. Hardy, W. E. Chase, and J. McCallum

Battelle Memorial Institute
Columbus, Ohio

INTRODUCTION

One of the principal objectives of research on molten-carbonate fuel cells[1-8] has been a battery which would operate on a carbonaceous fuel and air. Natural gas has been of special interest because of its low cost and wide availability.[1,3,7,9] However, in the references cited it has been recognized that hydrocarbons do not supply much current when used directly in the fuel cell. There must be a preceding chemical step such as steam reforming or partial air oxidation to yield electrochemically active species, predominantly hydrogen and carbon monoxide. The requirements for effective steam reforming in a fuel cell were discussed in a previous paper,[8] and the advantages of carrying out the steam reforming on the anode were described.

Three advantages are realized by steam reforming natural gas directly on the anode:

(1) Good heat exchange between the exothermic electro-
chemical oxidation and the endothermic steam-
reforming reaction.

(2) Less steam required because product steam from
electrochemical oxidation of hydrogen is
available.

(3) More extensive conversion of methane because
products (H_2 + CO) are being consumed.

The possibility of realizing these advantages led to the first goal of electrochemical research. The goal was to obtain both reforming and electrochemical oxidation on the anode.

THE DOUBLE-DUTY-ANODE CONCEPT

The idea of carrying out steam reforming on the anode itself has been proposed by previous workers. Linden and Schultz suggest it in a patent,[10] and Schultz et al.[11] describe results of some reforming experiments with methane-steam mixtures on nickel battery plaques. Sandler[4] described results of experiments with mixtures of natural gas and steam reformed in a separate catalyst chamber in contact with the cell. Schultz's

data indicated that at 730 C, 15 mole percent hydrogen would be found in a mixture reformed on a nickel battery plaque, and 12 percent would be found when reforming on the electrode holder alone. The equilibrium composition is about 75 percent hydrogen. Thus, nickel battery plaques are not particularly effective. Sandler reported almost complete (i.e., equilibrium) conversion of methane to hydrogen on his unspecified catalyst at 580 C.

The performance of all-nickel porous bodies as steam reformers might be improved by forcing the steam-methane mixture through the pores of the coarse layer rather than simply passing the gas mixture along one face of the porous plaque and allowing the mixture to diffuse into the reaction zone. It was to obtain this "forced-by" operation that the double-duty anode shown in Figure 1 was designed. The term "forced-by" is used to distinguish this mode of fuel feed from other modes such as diffusion, "blow-through", and "dead-end".

The electrode is designed for use with a free electrolyte; therefore, it is a two-layer, double-porosity electrode. That is, there is a fine-pore layer which is flooded with electrolyte during operation, sealing one face of the coarse layer against gas leakage. By sintering the other face of the coarse layer to the electrode holder, a gas passage is formed so that fuel gas introduced at one edge of the electrode is forced through the coarse layer parallel to the electrolyte-gas interface and out the opposite edge. The use of forced flow requires that pressure drop be considered. For long flow paths, it would be impossible to maintain the meniscus in the fine layer near the exit edge without exceeding the bubble pressure near the inlet. A rule of thumb adopted for designing electrodes was that the pressure drop between the inlet and exit edges should not exceed 10 percent of the bubble pressure of the fine-pore layer.

To meet the pressure drop requirements for large-area electrodes, a holder was designed which provided short flow paths without restricting the overall dimensions of the electrode. This design is shown in Figure 2. The fuel inlet and outlet channels are interlaced to force the methane-steam mixture through a section of the coarse layer.

OPERATIONAL LIMITS FOR DOUBLE-DUTY ANODE

Most fuel batteries to be economically successful must convert a large percentage of the fuel to electricity. This requires both extensive conversion of fuel to products and high electrochemical efficiency. While much emphasis has been placed on the latter condition (i.e., voltage efficiency), many investigators seems to have neglected, so far, the first requirement (i.e., extensive conversion). When the products of the electro-chemical reaction are gases, not only does dilution of the fuel occur, but the products reduce the reversible potential as their concentration increases.

This was well emphasized by Broers and Ketelaar[12] and by Chambers and Tantram,[3] who showed the effect of extent of conversion on the theoretical voltage of a cell.

Equilibrium gas compositions were calculated for each cell in a six-cell series-fed module (see Reference 8 for model). The calculated compositions for a 1:1 methane-steam mixture are given in Figure 3. It is apparent that most cells will be supplied with H_2 + CO if adequate reforming occurs. Double-duty anodes were operated on the composition corresponding to 70 percent electrochemical oxidation. This composition was designated "lean fuel gas". In the six-cell modules, the electrochemical consumption was projected as 84 percent; therefore, the last of the six cells must consume about half of the fuel value supplied to it. The goal established was 100 ma/sq cm at a potential more negative than -0.78 volt versus ORE* with 50 percent consumption of fuel. (The goal was also established on the basis of the design study.[8]) This potential was chosen because nickel is thermodynamically stable to oxidation according to the reaction

$$Ni + 1/2 \ O_2 \rightleftharpoons NiO$$
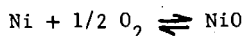
at potentials more negative than -0.78 volt versus ORE when $a_{NiO} = 1$ (i.e., when the melt is saturated with NiO) and no other reactions occur.

The potentials calculated (assuming equilibrium) for the fuel mixture entering several cells are given in Table 1. Thus, the limitations imposed on the potential of the anode in the sixth cell by gas composition

TABLE 1. OPEN-CIRCUIT POTENTIAL OF FUEL GAS MIXTURES

Cell (of 6)	Open-Circuit Potential,[a] at 1.4 Atm, vs ORE
1 entering	-1.22
4 entering	-0.98
6 entering ("Lean Fuel Gas")	-0.91

(a) See footnote, page 5, for description of Oxygen Reference Electrode (ORE).

and by the nickel corrosion potential leave only 0.13 volt for polarization.

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* Unpublished results. "ORE" is the Oxygen Reference Electrode, a reproducible, simple reference electrode for use in molten carbonates. It consists of a platinum wire spiral partially immersed in molten carbonate and bathed with a mixture of 70% CO_2 and 30% O_2. With proper construction and special attention to isolation of the electrolyte chamber from the bulk electrolyte, potentials are within 5 vf of the thermodynamically calculated values. It is reversible within the loading limits of a potentiometric recorder. In principle, this electrode is like those described by Stepanov and Trunov[13] and by Janz and Saegusa.[14]

OPERATION OF THE DOUBLE-DUTY ANODE ON A
LEAN FUEL GAS MIXTURE

To establish that the proper flow pattern could be achieved, electrodes were operated on fuel mixtures containing hydrogen and carbon monoxide before using methane-steam mixtures. Experiments on stability of the forced-by mode were combined with experiments to determine the extent of the fuel utilization.

First experiments were performed with 2-sq-cm electrodes mounted in a holder of the type illustrated in Figure 4. The fuel gas was introduced at the arc-shaped recess on one side and was removed at the recess on the opposite side. Stability of the forced-by mode was established in several experiments where current densities up to 100 ma/sq cm were obtained at -0.78 volt versus ORE. Occasional flooding of the anode occurred when fuel pressure dropped accidentally or intentionally. Flooding was readily corrected by closing the exit line to force electrolyte out of the coarse-pore layer. No permanent loss of performance resulted from flooding. Thus, stable electrode operation is possible with the forced-by mode.

Most of the electrodes were operated for only a few hours at a given performance level to establish that the mode of operation was stable. Some failures occurred, resulting in loss of gas pressure. Failures were traceable to poor bonding of the electrode to the holder or of the coarse layer to the fine layer. But, satisfactory long-term performance was indicated by operating an anode for 11-1/2 days. Initially the electrode and associated tubing system showed little leakage, but at the end of 11-1/2 days the leakage of gas into the melt had become too great for further results to have practical significance. Performance remained the same throughout except during one purging required to remove a flooding condition. On lean fuel gas (18 percent H_2 + CO) the current density was 75 ma/sq cm at -0.80 volt versus ORE. Fifty to sixty percent of the fuel value was converted electrochemically throughout the 11-1/2-day operation. This established that good fuel utilization could be obtained along with adequate performance.

Cause of the gas leakage can be seen on the photograph in Figure 5. Two types of failure are apparent. The separation in the coarse layer seen in the section is responsible for the large bulge in the center. With active fuels which do not require steam reforming, separation has little effect on electrode performance. Separation is a mechanical problem and can be corrected by improved sintering technique and by the use of a mechanical support in the form of a honeycomb alumina separator between electrodes in a cell which reduces the unsupported span of the sintered structure.

Pockmarks and the small mounds of powder which appear predominantly at the edge of the electrode were the sites of gas leakage. The location of pits near the exit side and of powder deposits near the inlet side suggests that the gradient in reduction potential from inlet to outlet sides is the cause of this type of failure. A gradient in the reducing power of the gas phase will result in a similar gradient in the melt within the pores of the anode. In more oxidizing regions nickel dissolves; in more reducing regions it deposits. Small particles, released from the porous matrix at one point, are suspended in the melt and are incorporated in the surface where nickel ions deposit. Despite the potential seriousness of the loss of material, two measures can be proposed to reduce the transfer of nickel:

(1) Provide more uniform gas distribution to minimize the reduction gradient across the anode.

(2) Overlay the anode surface with a fine mesh screen to retain particles loosened by dissolution of nickel. Electroformed nickel screens of 1000 lines per inch are available and provide the equivalent of a specimen prepared by powder metallurgy with large particle-particle contact. Such screens have given satisfactory performance in short-time experiments where the screen was used as the fine-pore layer.

During the operation of this small (2-sq-cm) anode, a mass spectrometric analysis was made of a sample of exit gas. On a dry basis, 95 percent of the sample was carbon dioxide. The hydrogen-to-carbon monoxide ratio was 1 to 1.6, indicating that even without a special water-gas shift catalyst about one-third of the current was derived from carbon monoxide. This result means that it will not be necessary to convert all the methane to hydrogen, and the water-gas shift need not be complete.

A laboratory-model fuel cell having 18-sq-cm electrodes was used for several experiments with lean fuel gas. The anode holder of Figure 2 was used in the laboratory cell. Problems of sealing the cell against electrolyte loss were avoided by dipping both electrodes into a pot of molten carbonate. A reference electrode was included in the setup for recording single electrode potentials. The best performance obtained with one of these anodes on lean fuel gas was 25 ma/sq cm at -0.78 volt versus ORE for about two days. The performance of the 18-sq-cm electrode was some-what low because of design and fabrication problems. Separation of the anode from the holder allowed fuel to bypass some sections of the electrode, resulting in a reduction of the effective area. Improvements in the design and fabrication are expected to bring the level of performance of the large anode up to that of the 2-sq-cm anode, or 100 ma/sq cm at -0.78 volt versus ORE.

STEAM REFORMING OF METHANE
ON ANODE STRUCTURES

After demonstrating that the double-duty anode would operate
satisfactorily in the forced-by mode and that the lean fuel gas reaching
the last of a series of six cells could sustain adequate current densities,
the next step was use of a methane-steam mixture in the double-duty anode.
A few experiments with nickel double-duty anodes revealed little activity
for steam reforming, in general agreement with the work of Schultz et al.

A suitable steam-reforming catalyst was sought for incorporation
into the nickel matrix. A survey of the literature revealed that a
suitable supported catalyst should be nickel on periclase (natural magnesium
oxide). Near-theoretical conversions of methane-steam mixtures to hydrogen
and carbon monoxide were reported.[15] Magnesium oxide is resistant to attack
by molten alkali carbonates, as is nickel in the fuel atmosphere.

Several trial compositions lead to a suitable mixture of nickel
and periclase powders which maintained structural integrity after pressing
and sintering. The compact consisted of 15 weight percent periclase and
85 percent nickel. Both were in the form of 100-micron powders. After
pressing and sintering under hydrogen, the compact was treated with nickel
nitrate solution and dried on a hot plate. The nickel nitrate was decomposed
and reduced simultaneously by heating in a hydrogen atmosphere to 760 C,
slightly above the operating temperature of the cell.

Prior to making fuel electrodes, small-scale steam-reforming
experiments were carried out with the catalyst-nickel powder mixture. The
small-scale reformer consisted of a 1/8-inch Inconel pipe (0.269-inch ID)
with brass tees silver soldered on each end. A 1/4-inch-OD Inconel tube
with 200-mesh nickel screen over the end was inserted into the pipe. The
pipe was oriented vertically in a 1-1/4-inch-diameter, 12-inch-long tube
furnace, and 1.4-cm layer of unsintered nickel nitrate-treated mixture
was packed onto the screen. The system was sealed well enough to keep the
leak rate at only 1 ml of hydrogen in 13 minutes at 6 psig. The ends of the
furnace were insulated, and heating tapes were used on the entrance line to
keep the temperature above 100 C.

The usual test procedure was as follows: (1) purge this reactor
with hydrogen, (2) heat to 760 C to decompose the nickel nitrate, (3) hold
1/2 to 1 hour at temperature to reduce the nickel oxide in the periclase,
(4) adjust the temperature to the value shown in Table 2, and (5) purge from
4 to 6 hours with methane-steam mixture at the pressure shown before sampling
the exit gas for analysis by mass spectrography.

The flow rate of the methane was adjusted to give a residence time of about 0.1 minute. A blank run was made with nickel powder in the reformer tube. Analytical results of these two experiments and the calculated equilibrium composition are given in Table 2.

TABLE 2. COMPOSITIONS OF MIXTURES RESULTING FROM
STEAM REFORMING OF METHANE

Condition	Pressure, psig	Temperature, C	CH_4	H_2	CO	CO_2	Percentage Reaction[a]
Theoretical Equilibrium	5.9	727	7.8	69.2	20.8	2.2	74.6
Nickel Powder	5.5	732	97.5	0.3	0.8	0.3	1.1
Catalyst Mixture	5.6	727	9.4	68.8	17.9	3.9	70

(a) Calculated from:[16]

$$\% \text{ reaction} = \left[1 - \frac{\% \text{ CH}_4}{\% \text{ CH}_4 + \% \text{ CO} + \% \text{ CO}_2} \right] 100.$$

Percentage reaction, calculated by the equation of Arnold et al.,[16] is a measure of methane reacted. The extent of the water-gas shift reaction cannot be measured by the equation. The results demonstrate the efficacy of the catalyst mixture for steam-reforming methane. A number of other experiments with differing amounts of catalyst and somewhat different temperatures and pressures also gave reaction percentages in the region of the theoretical values. These other experiments support the validity of the conclusion that the catalyst mixture is effective. The short residence time permits use of a 0.05 to 0.06-inch-thick coarse layer in an anode operating at 100 ma/sq cm. A small double-layer anode containing 15 weight percent catalyzed periclase in the coarse layer was also prepared. It was a structurally integral disc after pressing and sintering.

SUMMARY

Experiments have shown the feasibility of obtaining good steam-reforming activity from a supported nickel steam-reforming catalyst. It has also been demonstrated that such mixtures can be incorporated in a structurally integral two-layer electrode.

Anodes were designed for dual-purpose operation in a free-electrolyte molten-carbonate fuel cell. The ability of the anode structure to function properly with the forced-by fuel flow mode was demonstrated. Stable operation at 100 ma/sq cm at -0.80 volt versus ORE was obtained with a fuel mixture containing only 18 percent hydrogen and carbon monoxide. Such operation demonstrates that adequate performance can be obtained while electrochemically oxidizing 85 percent of the fuel value in a methane-steam mixture as required for the battery model discussed in an earlier paper. Further work is needed to establish long-time performance of the double-duty anode with methane-steam mixtures.

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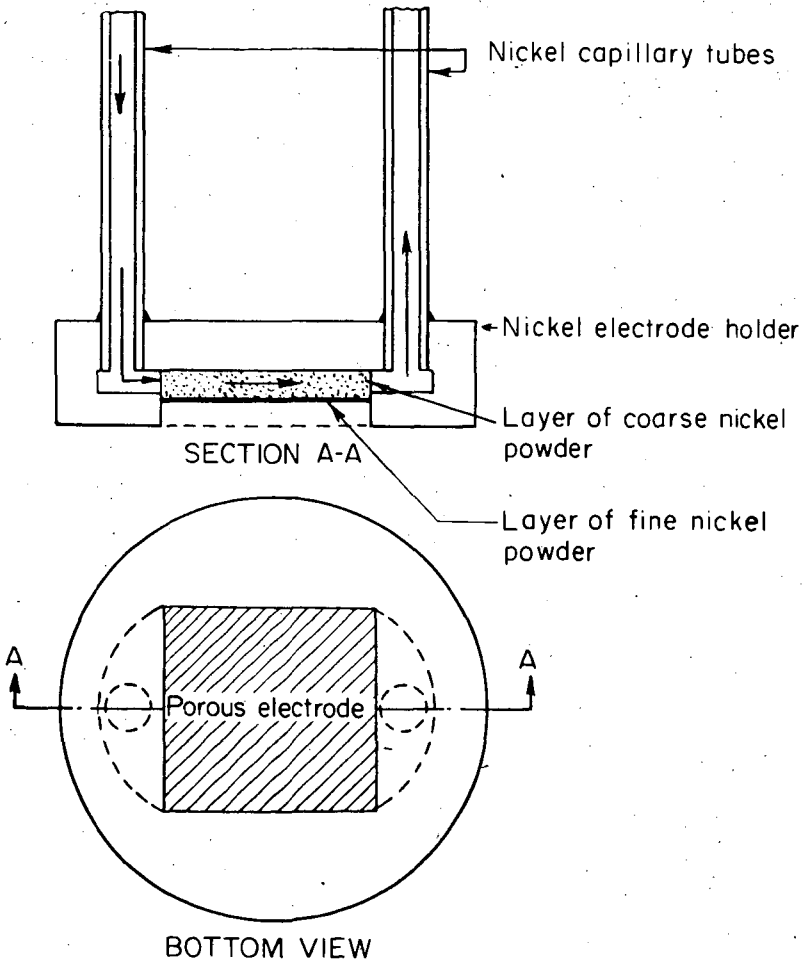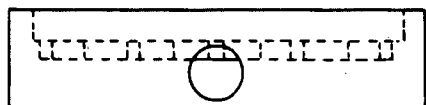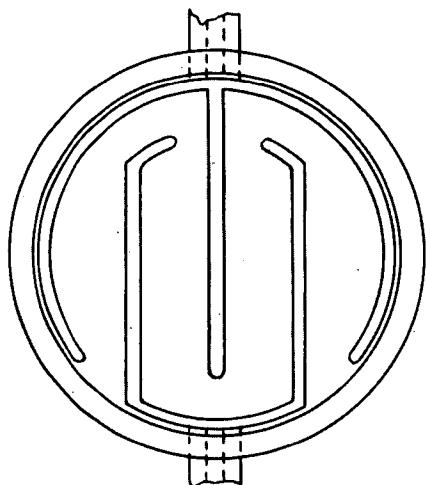
FIGURE 1. DOUBLE-DUTY ANODE DESIGN SHOWING FORCED-BY MODE.
(WHEN COARSE LAYER CONTAINS CATALYST THE ELECTRODE
PERFORMS BOTH FUNCTIONS, STEAM REFORMING OF METHANE
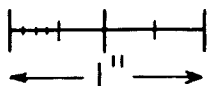AND ANODIC OXIDATION OF FUEL.)

Anode Holder

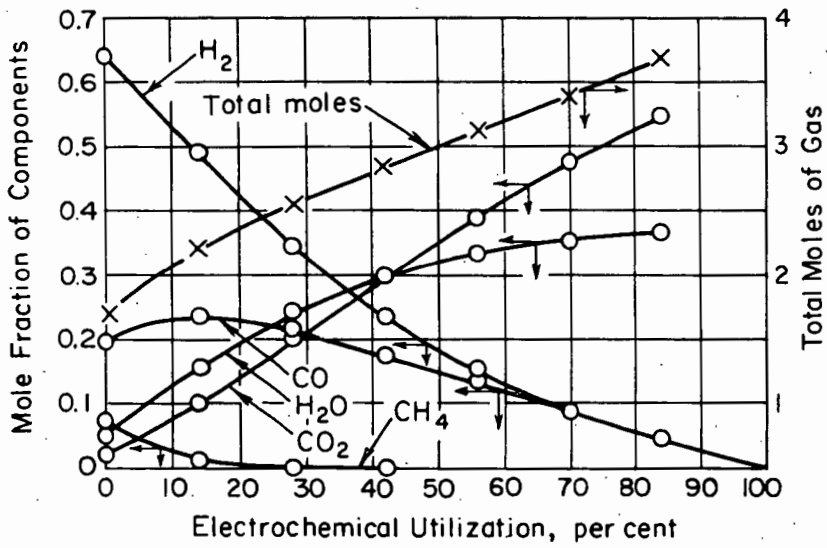FIGURE 2. HOLDER FOR LARGE DOUBLE-DUTY ANODES. ELECTRODE AREA
18 SQ CM.

FIGURE 3. CALCULATED EQUILIBRIUM GAS COMPOSITION IN A FUEL BATTERY SUPPLIED WITH 1:1 METHANE:STEAM MIXTURE AT 1000 K AND 1.4 ATMOSPHERES.
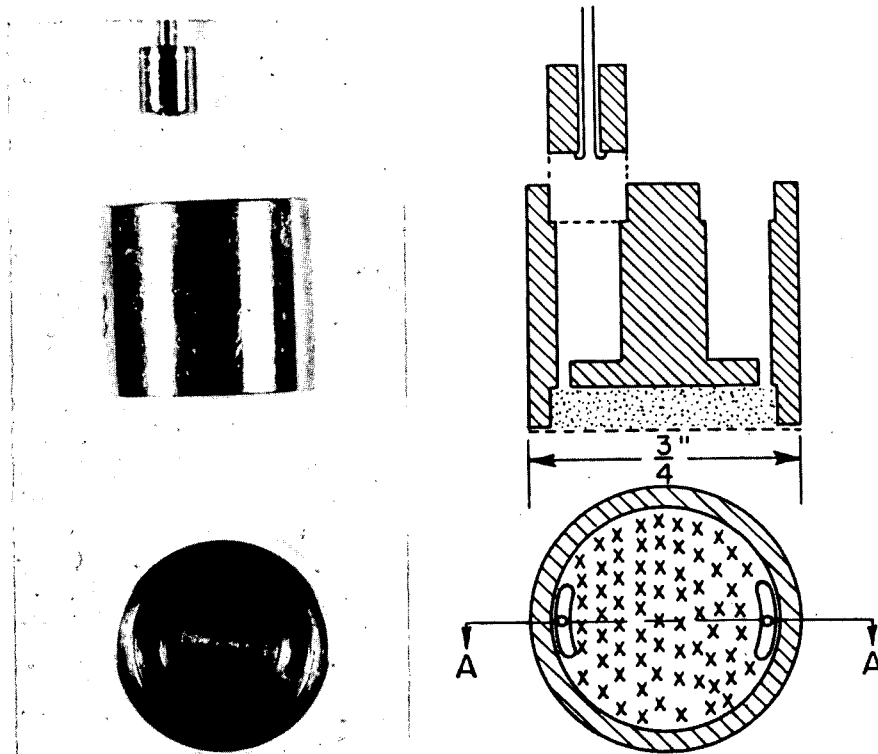
FIGURE 4. DETAILS OF 2-SQ-CM ANODES. ONE GAS INLET
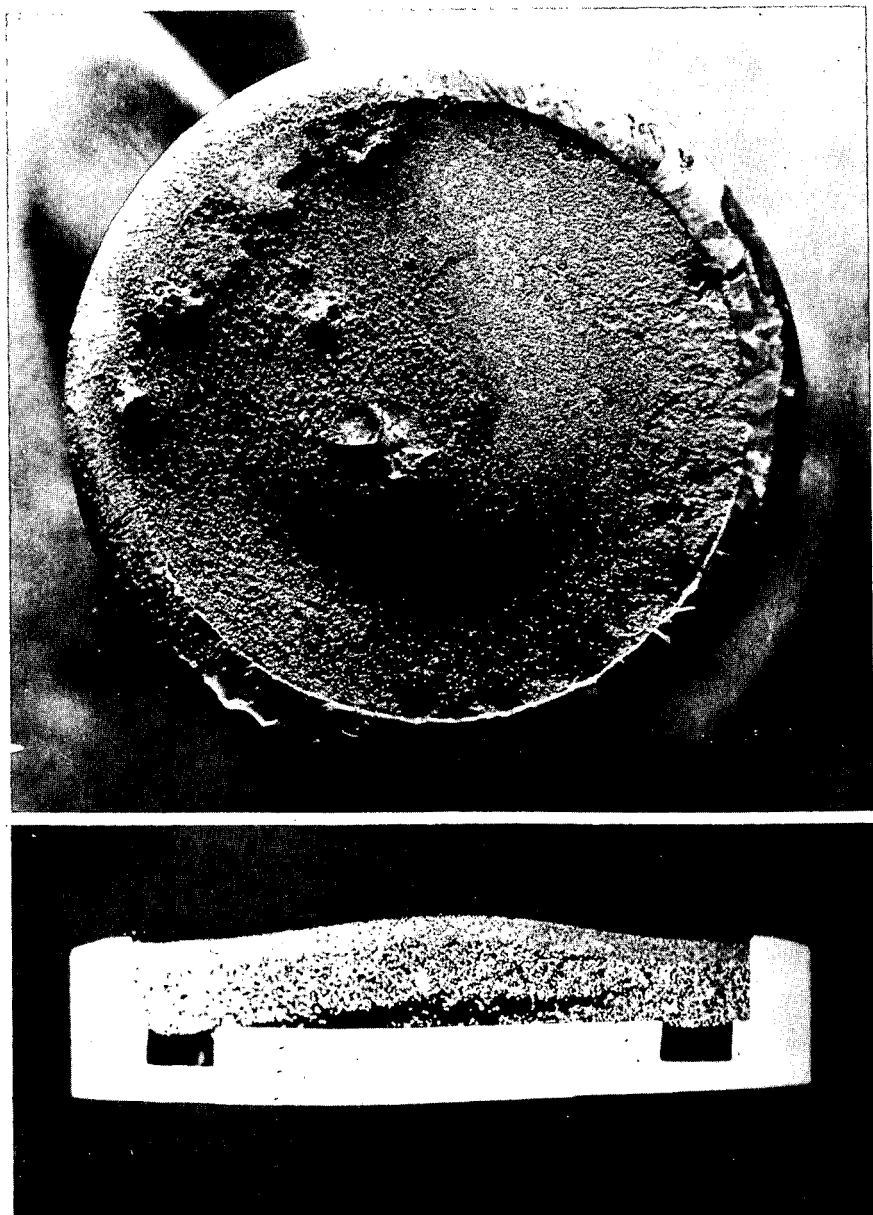TUBE WITH FERRULE IS SHOWN.

FIGURE 5. APPEARANCE OF A 2-SQ-CM ANODE AFTER 11-1/2
DAYS OF OPERATION ON LEAN FUEL GAS.